

## Co-pyrolysis of pine nut shells with scrap tires

Suat Uçar <sup>a,\*</sup>, Selhan Karagöz <sup>b</sup>

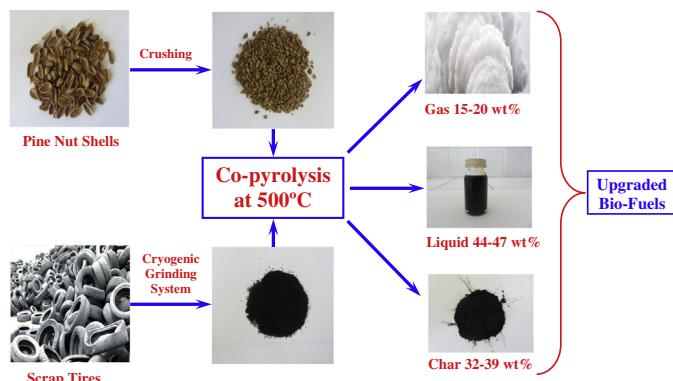
<sup>a</sup> Chemistry Technology Program, Izmir Vocational School, Dokuz Eylül University, 35160 Izmir, Turkey

<sup>b</sup> Department of Polymer Engineering, Faculty of Technology, Karabük University, 78050 Karabük, Turkey

### HIGHLIGHTS

- Co-pyrolysis of pine nut shells with scrap tires was carried out at 500 °C.
- The co-pyrolysis process improved the characteristics of all pyrolysis products.
- Biomass-derived oil can be upgraded via co-pyrolysis of biomass with scrap tires.
- The chars from co-pyrolysis have potential to be used as a commercial solid fuel.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 4 May 2014

Received in revised form 3 July 2014

Accepted 24 July 2014

Available online 5 August 2014

#### Keywords:

Biomass

Scrap tires

Pyrolysis

Upgrading

### ABSTRACT

The co-pyrolysis of pine nut shells (PNS) with scrap tires (ST) at different blend ratios was carried out at 500 °C. The addition of ST into PNS in the co-pyrolysis process not only increased bio-oil yields but also improved bio-oil characteristics when compared with the pyrolysis of PNS. The carbon content in bio-oils from all PNS/ST blend ratios was higher and oxygen content was lower than that of PNS-derived oil. This is an indication of the improved characteristics of bio-oils from the co-pyrolysis of biomass with scrap tires. The blend ratio in the feedstock of co-pyrolysis had a significant effect on the product distributions and physico-chemical properties of bio-oils. When heating values of bio-oils produced from the pyrolysis of PNS were compared with bio-oils obtained from the co-pyrolysis of PNS with ST, the addition of ST into PNS led to increase heating values of bio-oils with the exception of PNS/ST (4:1)-derived bio-oil. In addition, the heating values of gas products and levels of hydrogen and hydrocarbons (from C<sub>1</sub> to C<sub>4</sub>) in the gas products from the co-pyrolysis of PNS/ST blends were higher than that of the pyrolysis of PNS. The heating values of chars produced from the co-pyrolysis of PNS/ST blends were found to be in the range of 31.1 and 32.9 MJ kg<sup>-1</sup>.

© 2014 Elsevier Ltd. All rights reserved.

### 1. Introduction

Chemical recycling of waste materials is indeed of scientific importance from the perspective of realizing effective waste man-

agement. Waste materials can be classified as fossil-based wastes and bio-based wastes. Scrap tires are one of the most important fossil-based wastes. Approximately 1.5 billion tires are produced in the world each year and they are usually discarded into the environment [1]. Bio-based wastes have great potential as a component of major renewable energy sources that can provide the world with an alternative to fossil fuels. Thus, the evaluation of scrap tires and

\* Corresponding author. Tel.: +90 232 301 26 13; fax: +90 232 420 51 81.

E-mail address: [suat.ucar@deu.edu.tr](mailto:suat.ucar@deu.edu.tr) (S. Uçar).



waste biomasses is very important in terms of environmental pollution and economic aspects. Pyrolysis is one of the most viable and commonly used thermochemical conversion technologies which can be applied to both fossil-based and bio-based wastes. Chemical recycling of scrap tires via pyrolysis is currently carried out at industrial scales in many countries. Many scientific works have been carried out in the last two decades that investigate the production of liquid fuels from scrap tires via pyrolysis [1–5]. The production of biofuels from bio-based wastes via pyrolysis has attracted much attention from the scientific community as it represents a renewable and alternative option for energy production. Bio-based wastes are important bioresources often used to obtain bio-fuels. Various biomass wastes such as rice husk [6], almond shell [7], castor seed [8], pistachio shell [9] and cashew nut shell [10] have been used as raw materials for the production of biofuels via pyrolysis. Moreover, various advanced pyrolysis technologies with different reactor configurations have been applied to the production of fuels using both scrap tires and biomass. Studies concerning both liquefaction of scrap tires and biomass to produce liquid fuel have been carried out using various types of reactors including the fluidized bed reactor [11–13], the spouted bed reactor [14–17], the cyclone reactor [18] and the ablative reactor [19–21]. Liquid yields produced from the pyrolysis of scrap tires and/or biomass varied depending on the type of the reactor used in the study [11–21]. The type of pyrolysis technology had also important effects on the liquid yield and composition of the biofuel. The pyrolysis technologies used for both the liquefaction of scrap tires and biomass include slow [22,9], fast [23,6] and vacuum pyrolysis [24,25,21].

Bio-oils produced from biomass materials are mainly composed of oxygenated hydrocarbons. The oxygen content of bio-oils usually varies from 45 to 50 wt% [26]. Due to high oxygen content in bio-oils, they cannot be directly used as fuel. Thus, the upgrading of bio-oils via either hydroprocessing or using deoxygenation and/or dearomatization catalysts is necessary. Recent studies showed that the upgrading of bio-oils is also possible via the co-pyrolysis of biomass with either polymers or scrap tires [27–30]. Brebu et al. reported on the co-pyrolysis of pine cones with synthetic polymers (polyethylene, polypropylene and polystyrene) at 500 °C [27]. It was found that the yields of experimental co-pyrolysis liquids were higher than those of theoretical yields due to the synergistic effect. In another study [28], the co-pyrolysis of LignoBoost® lignin with synthetic polymers (polyethylene, polypropylene, polystyrene and polycarbonate) was carried out at 500 °C in order to investigate the interactions between LignoBoost® lignin and polymers. The addition of synthetic polymers into LignoBoost® lignin led to an increase in the yields of bio-oils. Both product distribution and the carbon number of bio-oils changed depending on the types of polymers added. In addition, the co-pyrolysis of almond shells with high density polyethylene was carried out at 500 °C [29]. The addition of high density polyethylene into almond shells not only increased bio-oil yields but also improved biofuel characteristics. Moreover, Martinez et al. investigated the co-pyrolysis of pine wood chips with scrap tires at 500 °C in a fixed bed reactor and a continuous auger reactor [30]. When the bio-oil produced from pine wood chips was compared with the bio-oil obtained from the co-pyrolysis of pine wood chips with scrap tires, the properties of bio-oil obtained from the co-pyrolysis improved remarkably.

As it is well known, the composition of lignocellulosic biomasses differs depending on the types of biomasses. Thus, it is still noteworthy to investigate the co-pyrolysis of different biomasses with scrap tires and to analyze product distributions and properties of all pyrolysis products. In this study, we carried out the co-pyrolysis of pine nut shells (PNS) with scrap tires (ST) at 500 °C. The different blend ratios of 1:1, 2:1, 4:1, 1:2 and 1:4 weight of

PNS and weight of ST were subjected to pyrolysis process. The effects of blend ratios on product distributions as well as the characteristics of pyrolysis products were investigated under identical conditions. Gas products produced from the co-pyrolysis of PNS with ST were determined. The properties of bio-oils obtained from the co-pyrolysis of PNS and ST were compared with commercial diesel and domestic fuel oils. The major compounds in tire-derived oil and bio-oils produced from the pyrolysis of PNS and co-pyrolysis of PNS and ST were identified. The chars produced from the co-pyrolysis of PNS and ST were also characterized as solid fuels.

## 2. Materials and methods

### 2.1. Materials

Pine nuts were collected from black pines (*Pinus nigra*) in Izmir, a city located in the western area of Anatolia in Turkey. Pine nut shells (PNS) were obtained after separation of pine nuts from the shells. PNS were milled and sieved to give an average particle size of 2 mm. The component analysis of PNS was performed according to a previous method in the literature [31]. Scrap tires were provided from the rubber recycling company (Akin Rubber) in Samsun-Turkey. Steel threads and the textile netting in the scrap tires were removed by the company. Then, the ST were grinded in a cryogenic medium and sieved to give an average particle size of 1.5 mm. The analysis of rubber contents in ST was carried out using a pyrolysis-gas chromatograph-mass spectrometer (Py-GC/MS) according to ASTM D3452-93 in Brisa Co, Izmit, Turkey. The proximate, ultimate and component analyses of PNS and ST are shown in Table 1. The chemicals used in the present study were of analytical grade and used as received from the company.

### 2.2. Pyrolysis procedure

Pyrolysis and co-pyrolysis experiments were performed at 500 °C under an inert atmosphere which was provided by the use of nitrogen gas. The experiments were conducted in a fixed bed reactor which is made of stainless steel reactor with a diameter of 6 cm and height of 21 cm. The required amounts of samples (totally 100 g) for the blend ratios of 1:1, 2:1, 4:1, 1:2 and

**Table 1**  
The properties of pine nut shells and scrap tires.

Feed	PNS	ST
<i>Proximate analysis (as received, wt%)</i>		
Moisture	7.85	0.88
Volatile matter	72.06	66.51
Fixed carbon	18.63	28.13
Ash	1.46	4.48
<i>Ultimate analysis (dry ash free basis, wt%)</i>		
C	52.04	87.04
H	6.95	7.94
N	0.29	0.75
S	0.08	1.46
O <sup>a</sup>	40.64	2.81
HHV <sup>b</sup> , (MJ kg <sup>-1</sup> )	18.5	38.6
<i>Component analysis (dry basis, %wt)</i>		
Extractives <sup>c</sup>	1.36	–
Hemicellulose	6.90	–
Lignin	48.97	–
Cellulose	41.42	–
Natural rubber (NR)	–	51
Styrene butadiene rubber (SBR)	–	39
Butadiene rubber (BR)	–	10

<sup>a</sup> By difference.

<sup>b</sup> Higher heating value.

<sup>c</sup> Toluene/alcohol (2/1) (v/v).

1:4 weight of PNS/ST were placed into the reactor. Then, the reactor was heated from ambient temperature to 500 °C at a heating rate of 5 °C min<sup>-1</sup> and held at this temperature for 1 h. The volatile products were swept to the collection flasks by nitrogen gas at a flow rate of 50 ml min<sup>-1</sup>. The liquid products were collected in the traps. Three condensers were used for this purpose. The first two condensers were cooled with a water–ice mixture. The cooling of the third condenser was completed with water. The pyrolysis experiments showed an acceptable standard deviation of 0.95 wt% for solid and liquid yields with three replicates.

After the pyrolysis experiments had been completed, the gas products were collected in a gas bag. The liquid and solid products were quantified separately. The amount of gas product obtained from pyrolysis and co-pyrolysis experiments was determined by difference. The liquid products consisted of bio-oil and aqueous phase. In the cases of the pyrolysis of PNS and the co-pyrolysis of PNS:ST (4:1), the bio-oil was separated from the aqueous phase by liquid–liquid extraction using diethyl ether since the aqueous phase contained tar fraction. The aqueous phase was then weighted. After the extraction process, the organic phase was dried with anhydrous sodium sulfate and filtered. After the evaporation of diethyl ether in the organic phase, bio-oils were obtained and quantified. In other runs, liquid products had two phases from the co-pyrolysis of PNS/ST blends with the exception of the PNS:ST (4:1) run. In these experiments, the aqueous phase was clearly separated from the bio-oil phase using a separating funnel and then it was weighted.

### 2.3. Characterization of the pyrolysis products

#### 2.3.1. Analysis of gas products

The gas products obtained from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends at 500 °C were collected in a gas bag and analyzed by an Agilent 7890A model gas chromatograph (GC). It has five valves, seven columns and three detectors (channels). The columns used in GC systems are as follows: Column#1: 0.5 M Hayesep Q 80/100 mesh, Column#2: 6 Ft Hayesep Q 80/100 mesh, Column#3: 6 Ft Molecular Sieve 5A 60/80 mesh, Column#4: 3 Ft Hayesep Q 80/100 mesh, Column#5: 8 Ft Molecular Sieve 5A 60/80 mesh, Column#6: 123–1015(cut) 2 m × 0.32 mm × 5 µm DB-1, Column#7: 19091P-S12 25 m × 0.32 mm × 8 µm HP-AL/S. The flame ionization detector (FID) analyzed the hydrocarbons from C<sub>1</sub> to C<sub>5</sub> in the first channel. CO<sub>2</sub>, CO, O<sub>2</sub> and N<sub>2</sub> in the gas products were analyzed by the first thermal conductivity detector (TCD1 with reference gas He) in the second channel. The second thermal conductivity detector (TCD2 with reference gas N<sub>2</sub>) only determined the hydrogen content in the third channel.

Gravimetric analysis was also applied for the determination of hydrogen sulfur (H<sub>2</sub>S) in the gas products. The specified concentration of lead nitrate (Pb(NO<sub>3</sub>)<sub>2</sub>) solution was placed into collection flasks. When the gas products were passed through the collection flasks containing lead nitrate solution, H<sub>2</sub>S in gas products was precipitated into lead sulfur (PbS). The reaction took place between H<sub>2</sub>S and Pb(NO<sub>3</sub>)<sub>2</sub> in traps. The precipitated PbS was then filtered with Whatman No. 1 filter paper. Finally, the precipitate was washed with distilled water, dried in an oven at 110 °C and weighted.

#### 2.3.2. Analysis of liquid products

The liquid products obtained from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends contained oil and aqueous phase. Several methods derived from the American Society of Testing and Materials (ASTM) were applied to determine the physico-chemical properties of pyrolysis oils after separation of pyrolysis oils from the aqueous phase.

The ASTM methods used for the analysis of pyrolysis oils were ASTM D4052-96 for the specific gravity, ASTM D445 for kinematic viscosities (using Tanaka KV-5S), ASTM D93 for flash points (using Tanaka APM-6) and ASTM D240-02 for heating values (using IKA C-2000 basic model calorimeter). In order to determine the water content in pyrolysis oils, Volumetric (according to ASTM E203-08) and Coulometric (according to ASTM D4928-12) Karl Fischer methods were applied using Mettler Toledo DL32 and DL31 titrators. The elemental content of pyrolysis oils and biochars were analyzed with a LECO CHNS 932 elemental analyzer according to ASTM D5291-96.

The analysis of pyrolysis oils was carried out by a gas chromatograph with a flame ionization detector (Hewlett–Packard 6890 series GC-FID). An HP-5 capillary column (30 m length × 0.32 mm diameter coated with cross-linked 5% phenyl methyl siloxane at a thickness of 0.25 mm) was used in the system. The GC oven was heated from 40 to 280 °C at heating rate of 5 °C min<sup>-1</sup> and held for 30 min at this final temperature. The estimations of cumulative volumes of heavy gas oil, light gas oil, heavy naphtha and light naphtha in pyrolysis oils were determined according to ASTM D2887 based on data obtained from the GC-FID analysis.

The gas chromatograph equipped with a mass detector (GC-MS) analysis of tire-derived oil and bio-oils from the pyrolysis of PNS and co-pyrolysis of PNS/ST (1:1) blend was carried out by an Agilent 6890N Network GC System with 5973 Network series mass selective detector. The column was a HP-5MS capillary column with a 30 m × 0.25 mm i.d., HP-5MS fused silica capillary with a film thickness of 0.25 µm. The GC initial oven temperature was 40 °C for 10 min; it was programmed to increase to 175 °C at heating rate of 2 °C min<sup>-1</sup> for 20 min; 200 °C at heating rate of 1 °C min<sup>-1</sup>; and then 250 °C at heating rate of 4 °C min<sup>-1</sup> for 20 min. The end of the column was directly introduced into the ion source of a 5973 Network series mass selective detector. The data acquisition system was completed with G1035A software using a NIST library database.

#### 2.3.3. Analyses of solid products and feedstock

Thermogravimetric analysis of PNS and ST was carried out using a thermogravimetric analyzer (Perkin Elmer Diamond TG/DTA). The TG runs were performed in a flowing nitrogen atmosphere with a flow rate of 200 mL min<sup>-1</sup>. The sample of PNS or ST (about 20 mg) was placed in a standard alumina crucible. The temperature was then increased from ambient temperature to 700 °C with a heating rate of 5 °C min<sup>-1</sup>.

The proximate analyses of PNS, ST and chars were carried out according to ASTM D3174-04 for ash analysis and ASTM D3175-89 for volatile matter. The elemental analyses of PNS, ST and chars were performed by a LECO CHNS 932 elemental analyzer according to ASTM D5291-96. The heating values of PNS, ST and chars were also determined using an IKA C-2000 basic model calorimeter according to ASTM D240-02.

## 3. Results and discussion

### 3.1. TG analysis and product distributions

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of PNS and ST are given in Fig. 1. The first weight loss in PNS occurred due to the release of moisture at between 25 and 100 °C. The small shoulder in the DTG profile was observed at approximately 275 °C due to the decomposition of hemicellulose. The main decomposition of PNS occurred around 320 °C which can be attributed to the decomposition of cellulose. The range of lignin decomposition was found to be wide and it began around 200 °C and ended at 500 °C. In the case of ST, two decomposition

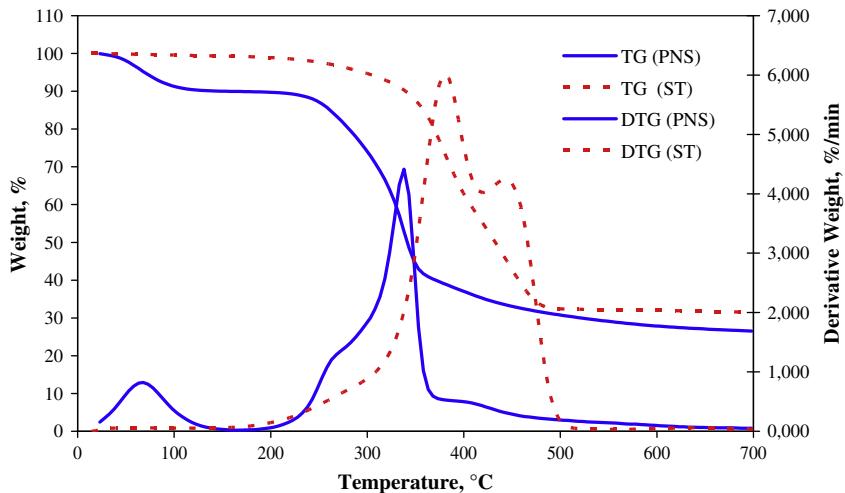


Fig. 1. TG and DTG curves of pine nut shells (PNS) and scrap tires (ST).

steps were observed. The first sharp peak is attributed to the decomposition of natural rubber and the second peak is related to the decomposition of styrene butadiene rubber and butadiene rubber. The decomposition started around 300 °C and finished around 500 °C. In a similar study, the co-pyrolysis of pine wood chips with scrap tires was carried out [30]. Pine wood chips and scrap tires at different blend ratios were analyzed using a thermogravimetric analyzer. It was shown that both pine wood chips and scrap tires were completely decomposed at 500 °C. Taking into account this previous report [30] and our TG analysis results, co-pyrolysis temperature was chosen as 500 °C.

Product distributions from the pyrolysis of PNS and ST and co-pyrolysis of PNS with ST at different blend ratios at a temperature of 500 °C are shown in Fig. 2. The gas yields produced from the co-pyrolysis of PNS/ST blends were found to be in a range from 15.4 to 20.1 wt%. The bio-oil yield produced from the co-pyrolysis increased when the ST ratio was raised in the blend of PNS/ST. The highest bio-oil yield was achieved with the blend at a ratio of PNS/ST (1:4). In contrast to the bio-oil yield, the aqueous phase yield obtained from the co-pyrolysis decreased when the ST ratio was increased in the blend of PNS/ST. The amount of char obtained from the co-pyrolysis experiments increased when the ST proportion of PNS/ST blends increased. This result can be attributed to the fact that ST have lower percentage of volatile matter and higher percentage

of fixed carbon than PNS (Table 1). For the purpose of comparison, experimental and calculated (theoretical) co-pyrolysis yields are also given in Fig. 3. The calculated liquid yields produced from the co-pyrolysis of PNS/ST blends were close to their corresponding experimental results. A previous study reported by Martinez et al. was concerned with the co-pyrolysis of pine wood chips with waste tires at 500 °C [30]. The calculated liquid yields were also close to their corresponding experimental values in the study.

As it can be seen in Fig. 2, the addition of ST into PNS led to a positive synergistic effect as bio-oil yields increased for all runs at different blend ratios. It is clearly seen that the yields of bio-oils obtained from the co-pyrolysis PNS/ST increased with addition of ST into PNS in comparison with PNS-derived bio-oil yield. The highest positive synergistic effect in the bio-oil was observed in the run with a ratio of PNS/ST (1:4). When the liquid yields (the sum of oil and aqueous phase yields) are taken into account, no significant synergistic effect was observed as the liquid yields were in the range between 44.3 and 47.0 wt% (Fig. 3.). In the study reported by Martinez et al., the co-pyrolysis of pine wood chips and scrap tires at different blend ratios (biomass/waste tires: 90:10 and 80:20) was carried out at 500 °C [30]. The experiments were carried out in a fixed bed and auger reactors. The results from the fixed bed reactor showed that the addition of scrap tires into pine wood chips had a negative synergistic effect for all blend ratios.

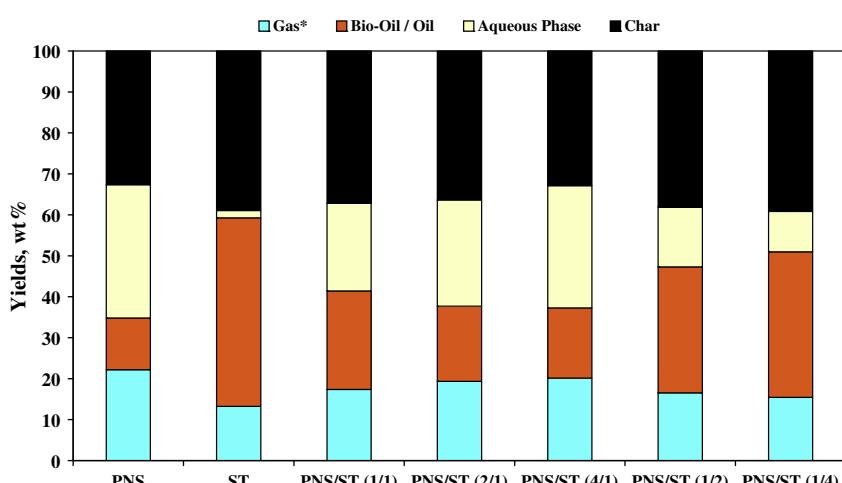


Fig. 2. Product distributions from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends at 500 °C (by difference).

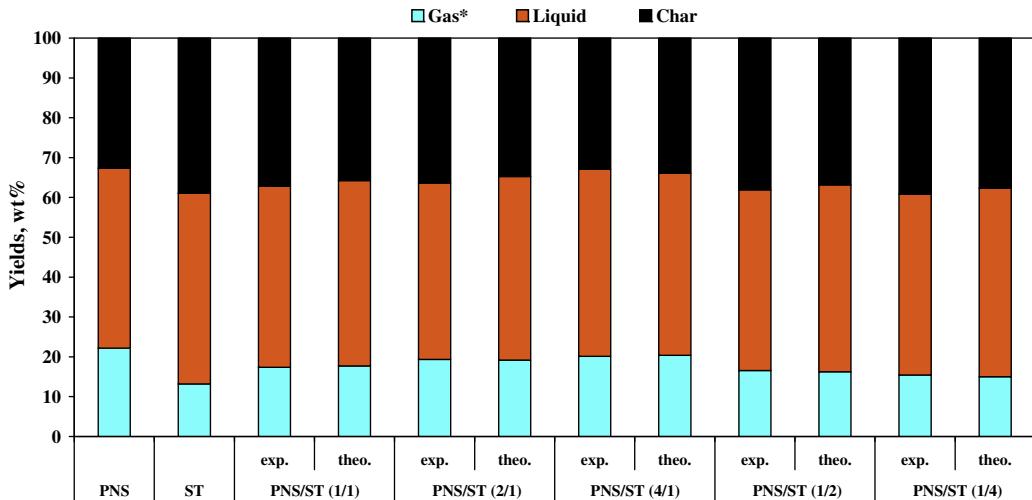


Fig. 3. Product yields and comparison of theoretical and experimental yields (' by difference; liquid: sum of bio-oil and aqueous phase).

The liquid yields slightly decreased with the addition of scrap tires into the biomass. In contrast to the fixed bed reactor, the use of the auger reactor produced a higher liquid yield at a biomass/waste tires ratio of 90:10 which represented a positive synergistic effect [30].

Previous studies concerning the pyrolysis of either waste tires or biomass showed that product distributions are strongly affected by the type of used pyrolysis technologies used with different reactor configurations. Martinez et al. reviewed the recycling of waste tires using different pyrolysis technologies [4]. The effects of experimental conditions (i.e. temperature, residence time, pressure and reactor type etc.) on pyrolysis products and liquid properties were reported, as well as the natural and rubber content in waste tires. The liquid yields ranged from 27.5 to 58.1 wt% depending on the type of reactor and temperature. In this study, the liquid yield from the pyrolysis of ST was found to be 47.84 wt% including the aqueous phase which was good enough in comparison with the existing literature. The review reported by Martinez et al. also showed that liquid yields varied even at the same temperature and reactor configuration due to the changing of other experimental variables [4].

As discussed above, liquid yields from the pyrolysis of biomass vary depending on the pyrolysis technology used as well as the biomass type. Generally speaking, liquid yields from the pyrolysis of biomass ranged from 34 to 75 wt% depending on the experimental conditions and the raw material [26,32]. Alvarez et al. investi-

gated the pyrolysis of rice husk in a conical spouted bed reactor at 400, 450, 500 and 600 °C [6]. The highest liquid yield was achieved at 450 °C. In another study, Puy et al. reported on the pyrolysis of forestry wastes in an auger reactor at the temperatures of 500, 550, 600, 700 and 800 °C with different residence times (1.5, 2, 3 and 5 min) and biomass flow rates (3.9, 4.8 and 6.9 kg h<sup>-1</sup>) [33]. The highest liquid yield was found to be 59 wt% and it was achieved under the following conditions: 500 °C temperature, 5 min residence time and 6.9 kg h<sup>-1</sup> mass flow rate. In the present work, the pyrolysis of PNS gave a liquid yield of 45.18 wt% which is comparable with data found in the literature.

Previous study dealing with the co-pyrolysis of pine wood chips and waste tires in a fixed bed reactor at 500 °C showed that the highest liquid yield level reached a value of 50 wt% at a blend ratio of 90:10 (biomass:waste tires) [30]. In the present study, the highest liquid yield was similarly found to be 47 wt% at a blend ratio of PNS/ST (1:4).

### 3.2. Characterization of gas products

The compositions of gas products produced from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends at 500 °C are shown in Fig. 4. It can be observed that the gas composition from the pyrolysis of PNS was composed of CO<sub>2</sub>, CO, C<sub>1</sub>–C<sub>4</sub> and H<sub>2</sub>. The major gas products were found to be CO<sub>2</sub> and CO. Previous studies also

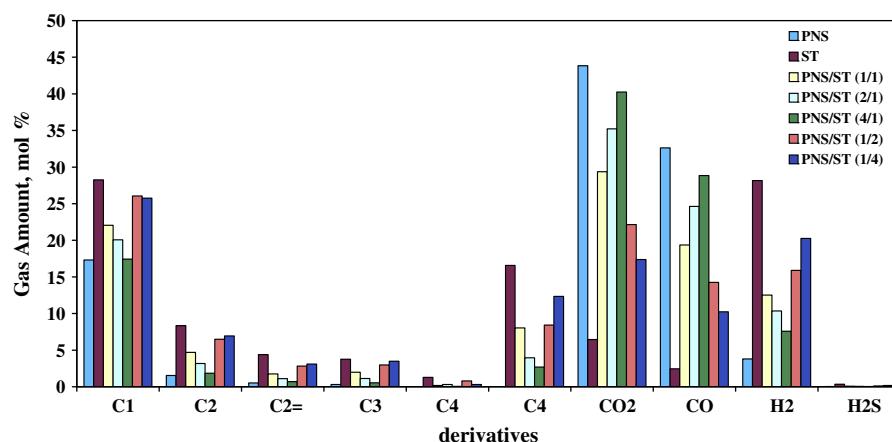


Fig. 4. Compositions of the gas products obtained from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends at 500 °C.

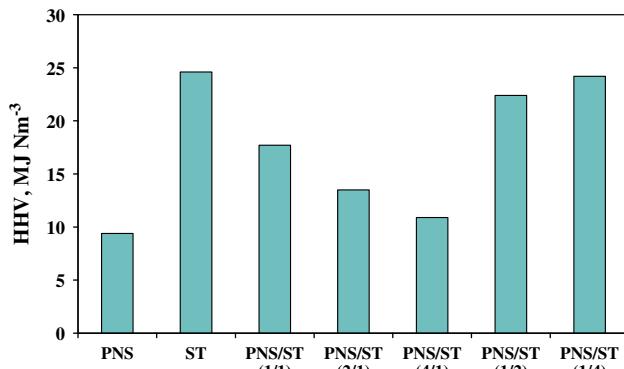


Fig. 5. Heating values of the pyrolysis and co-pyrolysis gas products.

showed that the pyrolysis of different biomasses produced a gas composition containing  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{C}_1\text{--C}_4$  and  $\text{H}_2$  [34–36].  $\text{CO}_2$  and  $\text{CO}$  were determined to be major gas products in these studies. Our experimental results are in a good agreement with these previous studies [34–36]. ST-derived gas products mainly consisted of  $\text{C}_1$ ,  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$  derivatives and  $\text{H}_2$ . In the case of the co-pyrolysis of PNS/ST, the addition of ST into PNS increased the contents of hydrogen and hydrocarbons (from  $\text{C}_1$  to  $\text{C}_4$ ) and decreased the contents of  $\text{CO}_2$  and  $\text{CO}$  in the gas products. Heating values of the pyrolysis and co-pyrolysis of gas products are shown in Fig. 5.

Table 2

Physico-chemical properties of oils produced from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends at 500 °C.

Feed PNS/ST ratio	PNS –	ST –	PNS/ST (1:1)	PNS/ST (2:1)	PNS/ST (4:1)	PNS/ST (1:2)	PNS/ST (1:4)	Commercial diesel	Domestic fuel oil (No.4)
Specific gravity at 15 °C, ( $\text{kg m}^{-3}$ )	1096.1	876.3	887.2	912.9	983.8	879.9	880.1	820–845	<998
Viscosity at 40 °C, (cSt)	7.96	1.99	3.01	3.73	7.88	2.28	2.38	2.0–4.5	5.5–24
Flash point, (°C)	<30	<30	<30	<30	<30	<30	<30	>55	>56
Water amount, (wt%)	7.89	2.78	0.47	0.36	6.91	0.18	0.12	<0.02	<0.5
HHV <sup>a</sup> , ( $\text{MJ kg}^{-1}$ )	25.6	44.2	42.2	41.3	25.7	43.2	43.4	~45	~43
<i>Elemental analysis, (wt%)</i>									
C	60.32	80.91	77.96	78.09	60.06	78.82	80.83	86.50	85.60
H	6.94	10.51	10.21	10.01	7.89	10.40	10.59	13.20	11.70
N	0.35	0.69	0.56	0.47	0.54	0.66	0.69	<1	<1
S	0.14	0.56	0.26	0.32	0.25	0.41	0.56	<0.7	<1
O <sup>b</sup>	32.25	7.33	11.01	11.11	31.26	9.71	7.33	–	<1

<sup>a</sup> Higher heating value.

<sup>b</sup> By difference.

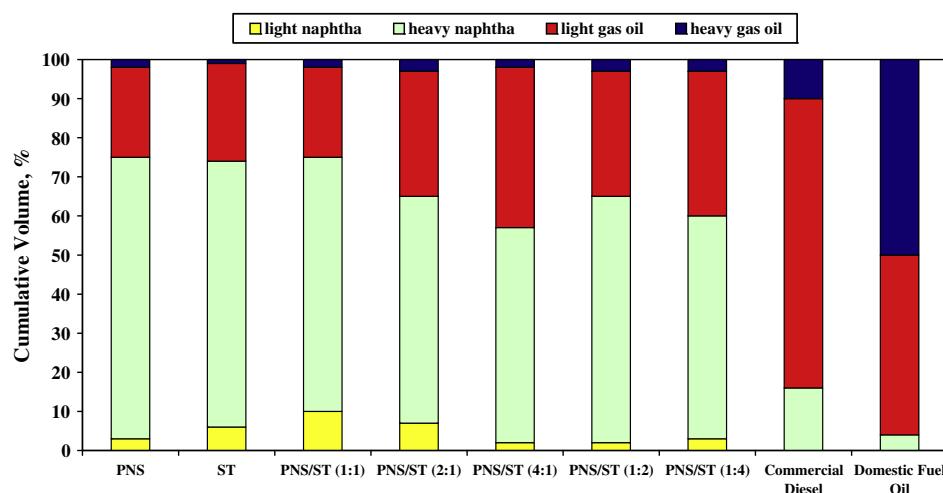


Fig. 6. Fractions of oils produced from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends at 500 °C.

Heating values of gas products from the pyrolysis of PNS and ST were 9.4 and 24.6  $\text{MJ Nm}^{-3}$ . Heating values of gas products from the co-pyrolysis of PNS/ST blends were found to be in a range from 10.9 to 24.2  $\text{MJ Nm}^{-3}$ . When the ST ratio in the PNS/ST blend was increased, the heating values of the co-pyrolysis gas products also increased. Similar results have been reported by Martinez et al. [30]. In their study, the researchers carried out the co-pyrolysis of pine wood chips (which is a different from the biomass used in the present study) with scrap tires at 500 °C. The heating values of gas products obtained from the co-pyrolysis of PNS/ST blends were higher than that of the PNS-derived gas products. This result indicates that the addition of ST into PNS in the co-pyrolysis process significantly improved the heating values of gas products.

### 3.3. Characterization of the bio-oils

The physico-chemical properties of tire-derived oil and bio-oils produced from the pyrolysis of PNS and co-pyrolysis of PNS/ST blends at different ratios at 500 °C are shown in Table 2. The physico-chemical properties of commercial diesel and domestic fuel oil are also incorporated into Table 2. It can be observed that the specific gravities of all bio-oils are higher than that of commercial diesel and lower than that of fuel oil. When other physico-chemical properties of bio-oils are taken into account (such as viscosities, water amounts, and heating values), the bio-oil properties are similar to those of fuel oil with the exception of PNS/ST (4:1)-derived oil. These results demonstrate that bio-oil properties

are significantly improved with the addition of ST into PNS in co-pyrolysis. Heating values of bio-oils from the co-pyrolysis of blends were ranged from 25.7 to 43.4 MJ kg<sup>-1</sup>.

The results of elemental analysis show that the addition of ST into PNS in the co-pyrolysis process led to an increase in carbon content and a decrease in oxygen content in bio-oils with the exception of PNS/ST (4:1)-derived oil. The values of the specific gravity, viscosity and water amount in bio-oil derived from PNS/ST (2:1) were found to be between the values from the pyrolysis

of PNS/ST (1:1) and PNS/ST (4:1). Interestingly, the carbon content in the bio-oil derived from PNS/ST (2:1) was slightly higher than that of the run of PNS/ST (1:1) which was not between PNS/ST (1:1) and PNS/ST (4:1). Both nitrogen and sulfur contents in bio-oils were found in acceptable levels. We can come to conclusion from these results that bio-oils were upgraded when the biomass was co-pyrolyzed with ST. However, it must be noted that the blend ratio of PNS/ST is important. A higher amount of ST rather

**Table 3**  
Major compounds in oils produced from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST (1:1) blend at 500 °C.

No	R.T. (min.)	Quality	Name of compounds	% Area		
				PNS	ST	PNS/ST (1:1)
<i>Benzene derivatives</i>						
1	4.34	94	Methylbenzene	0.83	2.17	2.70
2	8.16	91	Ethylbenzene	–	1.57	1.55
3	8.81	91	1,4-Dimethylbenzene	2.50	2.19	2.34
4	9.91	97	Styrene	–	0.85	0.93
5	10.02	95	1,3-Dimethylbenzene	0.26	0.64	0.74
6	12.29	81	(1-Methylethyl)benzene	–	0.57	0.40
7	16.13	95	1-Ethyl-2-methylbenzene	0.45	1.92	1.95
8	16.45	76	Propylbenzene	–	0.64	0.40
9	17.43	70	α-Methylstyrene	–	0.95	0.90
10	18.44	95	1,2,3-Trimethylbenzene	–	1.35	0.47
11	27.84	95	1-Methyl-4-(1-methylethyl)benzene	–	0.93	0.39
12	35.95	91	2-Ethenyl-1,4-dimethylbenzene	–	0.75	0.68
<i>Phenols</i>						
13	19.39	93	Phenol	1.29	–	–
14	25.29	96	2-Methylphenol	0.97	–	0.36
15	27.05	94	2-Methoxyphenol	11.09	–	2.02
16	31.52	96	2,4-Dimethylphenol	0.67	–	0.23
17	33.51	94	2-Methoxy-3-methylphenol	0.73	–	–
18	35.10	97	2-Methoxy-4-methylphenol	9.15	–	1.92
19	36.64	95	1,2-Benzenediol	2.97	–	–
20	41.02	91	4-Ethyl-2-methoxyphenol	7.91	–	1.74
21	42.80	96	4-Methyl-1,2-benzenediol	1.37	–	–
22	43.18	90	2-Methoxy-4-vinylphenol	2.32	–	–
23	46.00	98	2-Methoxy-3-(2-propenyl)phenol	1.09	–	0.31
24	46.65	91	2-Methoxy-4-propylphenol	4.19	–	0.66
25	49.14	98	(E) 2-Methoxy-4-(1-propenyl)phenol	4.47	–	0.54
<i>Terpenes</i>						
26	23.08	94	D-Limonene	–	17.66	17.34
<i>Olefins</i>						
27	6.32	90	1,3-Dimethylcyclohexene	–	0.67	0.69
28	14.05	70	2,5,6-Trimethyl-1,3,6-heptatriene	–	0.80	0.69
29	19.87	95	cis-2,6-Dimethyl-2,6-octadiene	–	0.83	0.72
30	21.36	70	1-Methyl-4-(1-methylethyl)-(R)-cyclohexene	–	2.56	1.78
31	23.43	93	5-Methyl-3-(1-methylethyl)-trans-cyclohexene	–	0.69	0.30
<i>Alkanes</i>						
32	4.02	90	1,1,2-Trimethyl-3-methylenecyclopropane	–	0.82	0.76
33	103.13	98	Heptadecane	–	0.56	0.45
<i>Aldehydes and ketones</i>						
34	7.14	95	Furfural	3.36	–	–
35	16.68	93	5-Methyl-2-furancarboxaldehyde	0.67	–	–
36	48.92	95	Vanillin	0.70	–	–
37	59.86	83	Hexadecanal	0.49	–	–
38	67.91	96	4-Hydroxy-2-methoxycinnamaldehyde	0.65	–	–
39	74.58	96	cis-9-Hexadecenal	1.92	–	–
40	74.99	94	E-9-Tetradecenal	1.27	–	–
41	5.07	87	Cyclopentanone	0.15	0.69	1.05
42	11.80	94	2-Methyl-2-cyclopenten-1-one	0.51	–	0.42
43	23.00	86	3-Methyl-1,2-cyclopentanedione	1.21	–	–
44	54.15	93	1-(4-Hydroxy-3-methoxyphenyl)ethanone	0.77	–	–
<i>Polycyclic aromatic hydrocarbons (PAH)</i>						
45	53.67	96	1-Methylnaphthalene	–	1.30	0.62
46	69.47	96	2,3-Dimethylnaphthalene	–	1.06	0.51
47	82.24	97	1,4,6-Trimethylnaphthalene	–	1.11	0.24
<i>Acids and acid derivatives</i>						
48	63.60	81	4-Hydroxy-3-methoxy-benzeneacetic acid	1.83	–	–
49	107.98	79	4-Hydroxy-3-methoxy-benzeneacetic acid methyl ester	1.25	–	–

**Table 4**

Proximate and ultimate analyses of chars produced from the pyrolysis of PNS or ST and co-pyrolysis of PNS/ST blends at 500°C.

Feed PNS/ST ratio	PNS –	ST –	PNS/ST (1:1)	PNS/ST (2:1)	PNS/ST (4:1)	PNS/ST (1:2)	PNS/ST (1:4)
<i>Proximate analysis (as received, wt%)</i>							
Volatile matter	12.44	4.08	7.89	9.16	10.58	6.99	6.21
Fixed carbon	83.41	84.63	84.23	84.49	84.05	84.36	83.92
Ash	4.15	11.29	7.88	6.35	5.37	8.65	9.87
<i>Ultimate analysis (dry, wt%)</i>							
C	89.47	75.20	80.26	83.94	84.97	79.56	78.86
H	3.09	1.29	2.04	2.46	2.72	1.95	1.51
N	0.59	0.45	0.65	0.68	0.62	0.71	0.61
S	0.13	2.56	0.73	0.65	0.37	0.95	1.26
O <sup>a</sup>	6.72	20.50	16.32	12.27	11.32	16.83	17.76
HHV <sup>b</sup> (MJ kg <sup>-1</sup> )	33.1	30.8	31.7	32.2	32.9	31.5	31.1

<sup>a</sup> By difference.<sup>b</sup> Higher heating value.

than PNS in PNS/ST blends improved the bio-oils when taking into account of both bio-oil yields and bio-oil properties.

The tire-derived oil and bio-oils produced from the pyrolysis of PNS and co-pyrolysis of PNS/ST blends at 500 °C were also characterized using GC-FID according to ASTM D2887. The fractions of tire-derived oil and bio-oils are shown in Fig. 6 and classified as light naphtha (<B.P.: 93 °C), heavy naphtha (B.P.: 93–204 °C), light gas oil (B.P.: 204–343 °C) and heavy gas oil (>343 °C) according to petroleum fractions. For the purpose of comparison, the distillation characteristics of commercial diesel and domestic fuel oil are also illustrated in Fig. 6. The highest light and heavy naphtha fraction of bio-oil produced from the co-pyrolysis of PNS/ST were obtained in the case of PNS/ST (1:1). When we compared PNS-derived oil with PNS/ST-derived oils at all ratios, the heavy naphtha fraction decreased and the light gas oil fraction either stayed same (PNS/ST 1:1) or increased (PNS/ST; 2:1; 4:1; 1:2; 1:4). Besides, all bio-oils produced from the co-pyrolysis of PNS/ST blends have lighter compounds than commercial diesel and domestic fuel oil. It should be noted that bio-oils contained oxygenated hydrocarbons. For this reason, the order of elution from the GC column will be different from their corresponding hydrocarbons. However, this result will not affect global comparison of bio-oils obtained from the co-pyrolysis of PNS/ST blends at different ratios.

Table 3 shows major compounds in PNS-derived oil, ST-derived oil and a representative of PNS-ST (1:1)-derived oil. Some of key compounds originated mainly from carbohydrate portion of the biomass were found to be furfural, 5-methyl-2-furancarboxaldehyde and 2-methyl-2-cyclopenten-1-one. Most of the identified compounds in PNS-derived oil were phenol derivatives which are mainly formed from the decomposition of lignin part of the biomass [35,37,38]. 2-methoxyphenol was observed as the major compound in PNS-derived oil. ST-derived oil was prominently composed of D-limonene, 1,4-dimethylbenzene, methylbenzene, ethylbenzene and styrene. The relative content of D-limonene was the highest in ST-derived oil. Similarly, previous studies regarding the pyrolysis of scrap tires showed that the formation of limonene in high yields is due to the thermal decomposition of natural rubber (polyisoprene) [39,40]. We could not observe any formation of new compounds in PNS-ST (1:1)-derived oil. D-limonene was identified as the major compound in PNS/ST-derived oil. The detected compounds in PNS/ST-derived oil resembled those of ST-derived oil. However, there were observed other compounds similar to PNS-derived oil such as 2-methylphenol, 2-methoxyphenol and 4-methyl-2-methoxyphenol which were mainly due to the decomposition of the biomass in the PNS/ST (1:1) blend. The compounds arisen from the ST in the PNS/ST blend were dominant and reduced biomass-derived compounds were observed in PNS/ST-derived oil. Some compounds such as aldehydes (furfural, 5-methyl-2-furancarboxaldehyde, vanillin, hexadecanal), ketones (3-methyl-1,2-cyclopentanedione,

1-(4-hydroxy-3-methoxyphenyl)-ethanone) and phenolic compounds (phenol, 2-methoxy-3-methylphenol, 2-methoxy-4-vinylphenol, 1,2-benzenediol) originated from the pyrolysis of biomass were not be observed in the PNS/ST-derived oil. The similar result has been reported by Martinez et al. [30]. They carried out the co-pyrolysis of pine wood chips with scrap tires at 500 °C in their study. They observed that the addition of waste tires to the biomass decreased the amount of aldehydes, ketones and phenolic compounds in bio-oil. Moreover, high aromatic content of PNS/ST (1:1)-derived oil may cause some handling and application problems at the industrial scale.

It should be noted that the analysis was not extended to whole liquid products. Aqueous phases from the co-pyrolysis of PNS with ST were not analyzed. As mentioned in the experimental section, bio-oils were recovered by liquid–liquid extraction using diethyl ether in the cases of the pyrolysis of PNS and the co-pyrolysis of PNS/ST (4:1) as the aqueous phase contained tar fraction. The extraction method used to obtain bio-oils may not be applicable at an industrial scale due to the requirement of high operational cost. Moreover, the aqueous phase was clearly separated from the bio-oil phase using a separating funnel in the other co-pyrolysis runs (PNS/ST ratios; 1:1, 2:1, 1:2, 1:4).

### 3.4. Characterization of the chars

Biochars are produced from either the pyrolysis of biomass or the co-pyrolysis of biomass with scrap tires and they are important products as they can be used either as solid fuel or as fertilizer [41,42]. The properties of chars from the co-pyrolysis of PNS with ST at 500 °C are shown in Table 4. The elemental composition of the chars changed depending on the PNS/ST blend ratio in the feedstock. The highest carbon and lowest oxygen amounts in chars were obtained at the ratio of PNS/ST (4:1). The addition of ST into PNS decreased carbon content and increased the oxygen and sulfur contents of all biochars produced from co-pyrolysis of PNS/ST blends when compared with the PNS-derived char. It should be noted that the reduction of the sulfur content in chars obtained from the co-pyrolysis experiments is more than proportional in relation to ST results. It is considered that cracking of organic sulfur compounds in chars occurred [43]. Some organic sulfur compounds were transformed into gases. The sulfur content of improved fuels should be within the legislated limit due to environmental concerns. The sulfur amounts in chars produced from the co-pyrolysis, which were in acceptable levels like bituminous, ranged from 0.37 to 1.26 wt%. The heating values of all chars produced from the co-pyrolysis of PNS/ST blends were found to be in the range of 31.1 and 32.9 MJ kg<sup>-1</sup>; these values are similar to commercial coal such as bituminous and anthracite.

## 4. Conclusion

The co-pyrolysis of pine nut shells with scrap tires was carried out at 500 °C. The addition of ST on PNS in the co-pyrolysis process had significant effects on both product distributions and bio-oil compositions when compared with the pyrolysis of PNS. The co-pyrolysis of PNS with ST led to increased bio-oil yields in comparison with PNS-derived oil yields. Bio-oils from PNS/ST blends at different ratios contained higher amounts of carbon and lower amounts of oxygen than that of the PNS-derived oil. Bio-oils were upgraded with the addition of scrap tires into the biomass. In addition, the chars produced from the co-pyrolysis of PNS with ST at different ratios can be used as a solid fuel. Taking into account these experimental results, it may be concluded that the co-pyrolysis of biomass with scrap tires is a viable way to produce an upgrade of bio-oils and chars as well as pyrolysis gases.

## Acknowledgements

The authors would like to thank Dokuz Eylül University for the pyrolysis set up being provided for Project (2006-KB FEN-010).

## References

- [1] Williams PT. Pyrolysis of waste tyres: a review. *Waste Manage* 2013;33(8):1714–28.
- [2] Oyedun A, Lam K, Fittkau M, Hui C. Optimisation of particle size in waste tyre pyrolysis. *Fuel* 2012;95:417–24.
- [3] Taylor R, Ray R, Chapman C. Advanced thermal treatment of auto shredder residue and refuse derived fuel. *Fuel* 2013;106:401–9.
- [4] Martinez JD, Puy N, Murillo R, García T, Navarro MV, Mastral AM. Waste tyre pyrolysis—a review. *Renew Sust Energy Rev* 2013;23:179–213.
- [5] Aylón E, Fernández-Colino A, Murillo R, Grasa G, Navarro MV, García T, et al. Waste tyre pyrolysis: modelling of a moving bed reactor. *Waste Manage* 2010;30(12):2530–6.
- [6] Alvarez J, Lopez G, Amutio M, Bilbao J, Olazar M. Bio-oil production from rice husk fast pyrolysis in a conical spouted bed reactor. *Fuel* 2014;128:162–9.
- [7] Caballero JA, Font R, Marcilla A. Comparative study of the pyrolysis of almond shells and their fractions, holocellulose and lignin. Product yields and kinetics. *Thermochim Acta* 1996;276:57–77.
- [8] Singh RK, Shadangi KP. Liquid fuel from castor seeds by pyrolysis. *Fuel* 2011;90(7):2538–44.
- [9] Apaydin-Varol E, Putun E, Putun AE. Slow pyrolysis of pistachio shell. *Fuel* 2007;86(12–13):1892–9.
- [10] Das P, Ganesh A. Bio-oil from pyrolysis of cashew nut shell—a near fuel. *Biomass Bioenergy* 2003;25(1):113–7.
- [11] Kaminsky W, Mennerich C, Zhang Z. Feedstock recycling of synthetic and natural rubber by pyrolysis in a fluidized bed. *J Anal Appl Pyrol* 2009;85(1–2):334–7.
- [12] Oasmaa A, Solantausta Y, Arpainen V, Kuoppala E, Sipilä K. Fast pyrolysis bio-oils from wood and agricultural residues. *Energy Fuels* 2010;24(2):1380–8.
- [13] Garcia-Perez M, Wang SX, Shen J, Rhodes MJ, Tian F-J, Lee W-J, et al. Fast pyrolysis of oil mallee biomass: effect of temperature on the yield and quality of products. *Ind Eng Chem Res* 2008;47(6):1846–54.
- [14] Lopez G, Olazar M, Aguado R, Bilbao J. Continuous pyrolysis of waste tyres in a conical spouted bed reactor. *Fuel* 2010;89(8):1946–52.
- [15] Lopez G, Olazar M, Amutio M, Aguado R, Bilbao J. Influence of tire formulation on the products of continuous pyrolysis in a conical spouted bed reactor. *Energy Fuels* 2009;23(11):5423–31.
- [16] Fernandez-Akarregi AR, Makibar J, Lopez G, Amutio M, Olazar M. Design and operation of a conical spouted bed reactor pilot plant (25 kg/h) for biomass fast pyrolysis. *Fuel Process Technol* 2013;112:48–56.
- [17] Amutio M, Lopez G, Artetxe M, Elordi G, Olazar M, Bilbao J. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. *Resour Conserv Recy* 2012;59:23–31.
- [18] Léde J, Broust F, Ndiaye FT, Ferrer M. Properties of bio-oils produced by biomass fast pyrolysis in a cyclone reactor. *Fuel* 2007;86(12–13):1800–10.
- [19] Léde J. Comparison of contact and radiant ablative pyrolysis of biomass. *J Anal Appl Pyrol* 2003;70(2):601–18.
- [20] Stanculescu M, Ikura M. Limonene ethers from tire pyrolysis Part 1: batch experiments. *J Anal Appl Pyrol* 2006;75(2):217–25.
- [21] Ba T, Chaala A, Garcia-Perez M, Roy C. Colloidal properties of bio-oils obtained by vacuum pyrolysis of softwood bark. Storage stability. *Energy Fuels* 2004;18(1):188–201.
- [22] Williams PT, Bottrell RP. Sulfur-polycyclic aromatic hydrocarbons in tyre pyrolysis oil. *Fuel* 1995;74(5):736–42.
- [23] Leung DYC, Yin XL, Zhao ZL, Xu BY, Chen Y. Pyrolysis of tire powder: influence of operation variables on the composition and yields of gaseous product. *Fuel Process Technol* 2002;79(2):141–55.
- [24] Roy C, Chaala A, Darmstadt H. The vacuum pyrolysis of used tires: end-uses for oil and carbon black products. *J Anal Appl Pyrol* 1999;51(1–2):201–21.
- [25] Garcia-Perez M, Chaala A, Roy C. Vacuum pyrolysis of sugarcane bagasse. *J Anal Appl Pyrol* 2002;65(2):111–36.
- [26] Bridgwater AV. Biomass fast pyrolysis. *Therm Sci* 2004;8(2):21–49.
- [27] Brebu M, Ucar S, Vasile C, Yanik J. Co-pyrolysis of pine cone with synthetic polymers. *Fuel* 2010;89(8):1911–8.
- [28] Brebu M, Spiridon I. Co-pyrolysis of LignoBoost® lignin with synthetic polymers. *Polym Degrad Stabil* 2012;97(11):2104–9.
- [29] Önal E, Uzun BB, Pütün AE. Bio-oil production via co-pyrolysis of almond shell as biomass and high density polyethylene. *Energy Convers Manage* 2014;78:704–10.
- [30] Martínez JD, Veses A, Mastral AM, Murillo R, Navarro MV, Puy N, et al. Co-pyrolysis of biomass with waste tyres: upgrading of liquid bio-fuel. *Fuel Process Technol* 2014;119:263–71.
- [31] Li S, Xu S, Liu S, Yang C, Lu Q. Fast pyrolysis of biomass in free-fall reactor for hydrogen-rich gas. *Fuel Process Technol* 2004;85(8–10):1201–11.
- [32] Akhtar J, Amin NS. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. *Renew Sust Energy Rev* 2012;16(7):5101–9.
- [33] Puy N, Murillo R, Navarro MV, López JM, Rieradevall J, Fowler G, et al. Valorisation of forestry waste by pyrolysis in an auger reactor. *Waste Manage* 2011;31(6):1339–49.
- [34] Horne PA, Williams PT. Influence of temperature on the products from the flash pyrolysis of biomass. *Fuel* 1996;75(9):1051–9.
- [35] Bertero M, Gorostegui HA, Orrabalís CJ, Guzmán CA, Calandri EL, Sedran U. Characterization of the liquid products in the pyrolysis of residual chañar and palm fruit biomasses. *Fuel* 2014;116:409–14.
- [36] Azargohar R, Jacobson KL, Powell EE, Dalai AK. Evaluation of properties of fast pyrolysis products obtained from Canadian waste biomass. *J Anal Appl Pyrol* 2013;104:330–40.
- [37] Oasmaa A, Kuoppala E. Fast pyrolysis of forestry residue. 3. Storage stability of liquid fuel. *Energy Fuels* 2003;17(4):1075–84.
- [38] Kim SJ, Jung SH, Kim JS. Fast pyrolysis of palm kernel shells: Influence of operation parameters on the bio-oil yield and the yield of phenol and phenolic compounds. *Bioresour Technol* 2010;101(23):9294–300.
- [39] Mastral AM, Murillo R, Callén MS, García T, Snape CE. Influence of process variables on oils from tire pyrolysis and hydropyrolysis in a swept fixed bed reactor. *Energy Fuels* 2000;14(4):739–44.
- [40] Pakdel H, Pantea DM, Roy C. Production of dl-limonene by vacuum pyrolysis of used tires. *J Anal Appl Pyrol* 2001;57(1):91–107.
- [41] Marris E. Putting the carbon back: black is the new green. *Nature* 2006;442:624–6.
- [42] Goyal HB, Seal D, Saxena RC. Bio-fuels from thermochemical conversion of renewable resources: a review. *Renew Sust Energy Rev* 2008;12(2):504–17.
- [43] Hu H, Fang Y, Liu H, Yu R, Luo G, Liu W, et al. The fate of sulfur during rapid pyrolysis of scrap tires. *Chemosphere* 2014;97:102–7.